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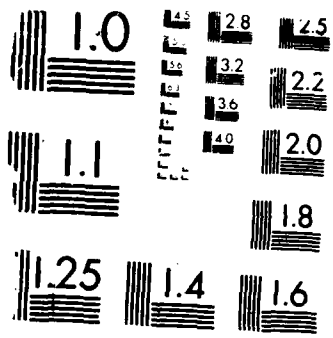

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CARBON RESIDUE STUDIES OF POLYPHENYL ETHERS AND ESTER-BASED LUBRICANTS USING A MICROCARBON RESIDUE TESTER

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A commercial microcarbon residue tester (MCRT) was used to measure the amount of carbon residue generated from ester-based lubricants with viscosities of 4 and 7.5 cSt and from the polyphenyl ethers 5P4E, 5P4E with an antioxidant additive, 4P3E and 3P2E. All of the lubricants showed significant volatilization at all temperatures with the polyphenyl ethers generally leaving residues which were less than 10 weight percent of the initial sample. An analysis of the weight percent residue as a function of location of the samples within the MCRT oven showed that a minimum of 6 sample vials distributed in either even or odd locations is needed to give reliable quantities of residue.

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PREFACE

This technical report was prepared for the Lubrication Branch, Fuels and Lubrication Division, Aero Propulsion Laboratory (APL), Air Force Wright Aeronautical Laboratories (AFWAL), Air Force Systems Command, Wright-Patterson Air Force Base, Ohio. The research was sponsored by the Air Force Office of Scientific Research/AFSC, United States Air Force, under Contract F49620-85-C-0013 during the period June 1986 to September 1986. Special acknowledgement is given to Phillip W. Centers who served as effort focal point for the project and to Chris Klenke and Bob Wright who provided technical assistance during the project.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF TABLES

SECTION I

INTRODUCTION

Lubricants for the next generation of turbine engines must be able to withstand more severe thermal and oxidative stress than current lubricants. These lubricants will be screened using a variety of physical, chemical and performance tests. Time and money could be saved if a simple laboratory test could eliminate undesirable lubricants before more expensive performance testing is done.

One important performance property of a lubricant is deposition tendency. Since carbon deposits within a turbine engine cause a series of problems that can ultimately lead to operational engine problems and increase maintenance requirements, the deposition tendency of a lubricant is very important. The microcarbon residue tester (MCRT) developed by Alcor, Inc., for use in American Society of Testing and Materials Test Method D-4530 has been employed for determination of carbon residue generated by several ester-based lubricants (Refs. 1 and 2). The purpose of this project was to extend that work to additional ester-based lubricants of different viscosities and to a series of polyphenyl ethers, which are potential lubricants for the new generation of turbine engines due to their thermal and oxidative stability (Ref. 3).

SECTION II

EXPERIMENTAL PROCEDURES AND EQUIPMENT

The MCRT-100, made by Alcor, Inc., of San Antonio, Texas, is a microprocessor controlled heating unit. One to 12 vials of 0.5 dram capacity can be placed in the oven and heated to 600°C at rates varying from 1°C to 50°C per minute. The oven chamber is continuously purged with air or nitrogen at gas flow rates of 150 cm^3 or 600 cm^3 per minute. Test conditions, such as rate of temperature increase, set-point (maximum) temperature, length of time at the set-point and gas flow rate, can be programmed into the microprocessor.

In each of the experiments in this study the oven temperature reached its maximum in 30 minutes with the gas flow set at 600 cm^3 per minute. The maximum temperatures, which ranged from 250°C to 400°C, were maintained for up to 50 hours. Cooling to room temperature required up to 3 hours. The gas flow rate was 150 cm^3 per minute during the constant temperature treatment and the cooling. All experiments used air as the purge gas.

Samples of 0.5 gram were placed into 0.5 dram vials which had been washed with soapy water, rinsed with distilled water and dried in an oven at 110°C. A Sauter RE 1614 balance was used to record the masses of the samples to the nearest 0.1 mg. The balance's uncertainty was 0.1 mg.

Actual sample temperatures were measured using a J-type iron-constantan thermocouple and a Leeds-Northrup millivolt meter. The thermocouple was channeled into the oven through the port leading to the trap and its tip was submerged in 0.5 g of the polyphenyl ether, 5P4E.

SECTION III

RESULTS AND DISCUSSION

1. Sample Temperatures

Bochartz (Ref. 1) showed that the temperature throughout the oven was uniform and that the temperature of the samples was about 10-14°C above that shown on the microprocessor display. The two units used in this work showed sample temperatures 18°C and 14°C higher than the display. The deviation from the display temperature was linear for the range of 280-400°C. Appropriate adjustments were made in the microprocessor set points so that both units operated at the comparable temperatures. The data reported here follow the practice of Bochartz in reporting the display temperature of MCRT unit #2 which is 14°C below the actual sample temperature.

Figure 1 shows the lag time between the MCRT temperature display and the actual sample temperature during the initial heating period. The sample reaches its maximum temperature about 20-25 minutes after the oven itself has reached its maximum.

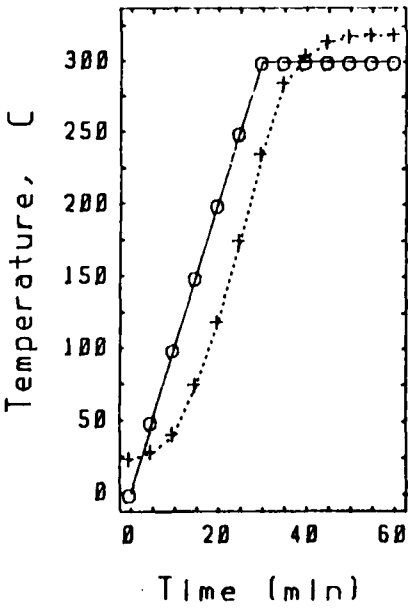


Figure 1. Plot of MCRT display temperature, o, and actual sample temperature, +.

2. Residue as a Function of Position in the Oven

Bochartz (Ref. 1) examined the effect of the location of a sample in the oven on the amount of residue produced. His study showed that at least 5 sample vials must be used in order to get reliable results. The data in this study were analyzed to determine the magnitude of the deviations from the mean for the samples in various locations. Comparisons were based on a percent deviation that was calculated by determining the average for a set of locations, subtracting that average from the mean of all 12 vials, and then dividing the difference by the standard deviation. Comparison was made with the standard deviation to compensate for the wide range of values for the standard deviations of the 41 experiments used.

The percent deviation was calculated for the following combinations of sample vial positions: even(odd), 1-3-5, 4-6-8, and 2-4-6-8-10. Table 1 summarizes the results.

Table 1. Percent Deviation as a Function of Vial Location

% Deviation Range	Number of Samples within the Range[a]			
	Even	4-6-8	2-4-6-8-10	1-3-5
0-10	9/7	1/4	4/6	3/3
11-20	5/2	2/0	5/5	1/1
21-30	5/7	2/3	4/4	3/2
>30	1/4	15/14	9/6	13/15

[a] The numbers represent the two MCRT units.

These data indicate that 6 samples in either even or odd positions give averages with good precision. Use of 5 samples in the 2-4-6-8-10 positions as recommended by Bochartz (Ref. 1) gives lower precision than the six sample approach. Use of fewer than 5 samples is not recommended.

Several experiments were completed with two or three different polyphenyl ethers in the oven simultaneously. No effect on the amount of residue produced was observed.

3. Ester-based Lubricants

Table 2 gives the data for the degradation for a series of ester-based lubricants.

Table 2. Weight % Residue, Ester-based Lubricants

Lubricant	Viscosity (cSt, 100°C)	MCRT (15 h, 300°C)	σ_x	Static Coker (315°C)
MIL-L-7808J*	3	8.49-13.72		
4 cSt MIL-L-7808 candidate	4	18.63	0.47	27.7
MIL-L-23699C*	5	21.15-27.47		
D-ENG-RD-2487 Sample 1	7.5	14.24	0.97	30.5
D-ENG-RD-2487 Sample 2	7.5	7.38	0.38	10.4

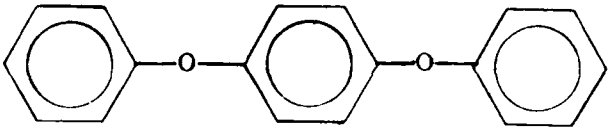
*Data from Bochartz (Ref. 1)

Bochartz (Ref. 1) reported data for the degradation of 14 different ester-based lubricants with the MCRT. MIL-L-7808J oils (viscosity 3 cSt at 100°C) yielded residues of 8.49 percent to 13.72 percent. MIL-L-23699C oils (viscosity 5 cSt at 100°C) yielded residues of 21.15 percent to 27.47 percent. The residue produced from the 4 cSt oil falls into the pattern of increasing residue with increasing viscosity. However, the two 7.5 cSt oils produced residues which were comparable to the residues generated from the 3 cSt oils. The lower amounts of residue formed in the MCRT from the 7.5 cSt oils are consistent with the static coker data for the same samples. This may be due to formulation differences in additives or basestock components

between these oils and the lower viscosity oils or possibly the products of the degradation are more volatile than those formed in the lower viscosity oils.

4. Polyphenyl Ethers

Polyphenyl ethers are compounds containing a number of benzene rings joined together via oxygen atoms. A shorthand notation for these compounds simply specifies the number of benzene rings and ether links. The structure shown below would be referred to as 3P2E. No attempt will be made in this



report to specify ortho, meta, and para bonding positions on the benzene rings. A detailed review of the structure, nomenclature, and properties of polyphenyl ethers can be found in Reference 3.

Tables 3, 4, and 5 give the data for the degradation of the polyphenyl ethers 5P4E, 4P3E and 3P2E, respectively. Figures 2 through 4 represent these data graphically.

Table 3. Weight % Residue, 5P4E

Time(hr)	325°C	σ_x	350°C	σ_x	375°C	σ_x	400°C	σ_x
5					57.36	1.90	19.43	1.14
7							5.45	0.83
10					21.09	1.87	4.83	0.53
15	74.32	1.80	44.61	2.97	5.52	0.48	3.76	0.29
20			26.85	1.79	5.01	0.37	2.99	0.33
25			9.40	1.57				
50	27.7	6.4						

Table 4. Weight % Residue, 4P3E

Time(hr)	275°C	$\sigma_{\bar{x}}$	300°C	$\sigma_{\bar{x}}$	310°C	$\sigma_{\bar{x}}$
5					69.61	1.27
10	80.62	0.57	54.48	1.98	39.96	2.11
15	71.71	0.61	34.37	1.96	12.93	0.78
20	61.88	0.75	14.26	2.83	0.48	0.03
25			0.60	0.09		
50	19.81	1.08				

Table 5. Weight % Residue, 3P2E

Time(hr)	250°C	$\sigma_{\bar{x}}$	275°C	$\sigma_{\bar{x}}$	300°C	$\sigma_{\bar{x}}$	325°C	$\sigma_{\bar{x}}$
5	83.62	0.40	35.33	0.53	14.88	0.17	5.73	0.21
10	64.59	0.90	19.29	0.33	14.85	0.13	4.91	0.23
15	47.63	1.00	15.44	0.51	14.25	0.13		
20	39.78	0.93	14.14	0.33	13.35	0.20	3.43	0.25
25			13.00	0.47	12.81	0.17		
30	27.19	1.01						
50	13.71	0.64						

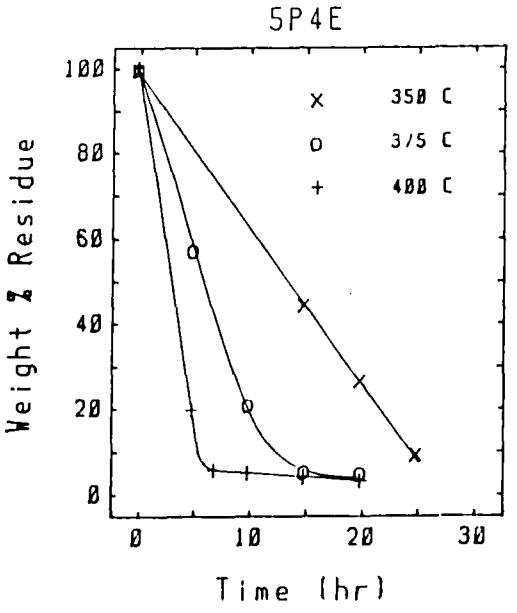


Figure 2. Weight % residue as a function of time, 5P4E.

Figure 3. Weight % residue as a function of time, 4P3E.

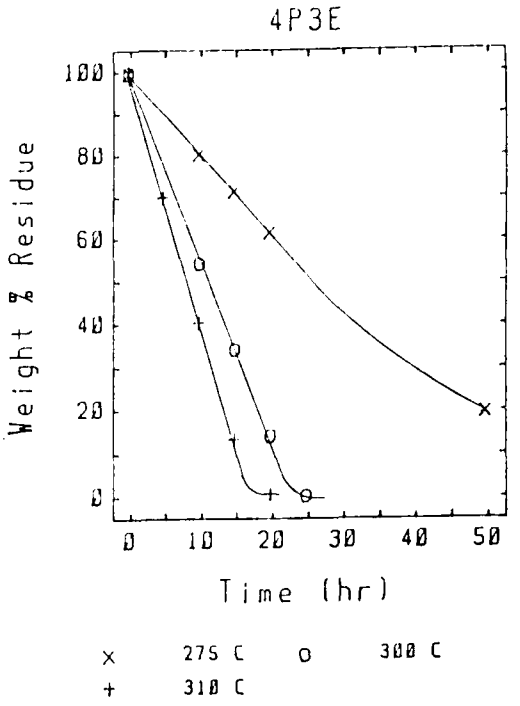
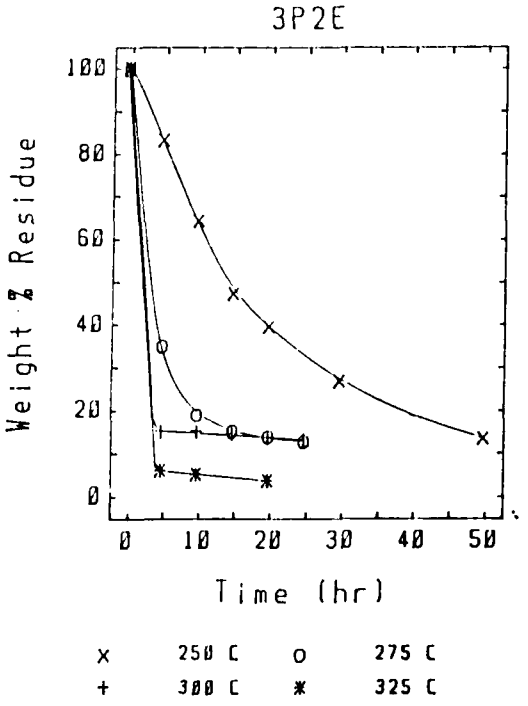


Figure 4. Weight % residue as a function of time, 3P2E.



Tables 3 through 5 and Figures 2 through 4 indicate that each of the polyphenyl ethers shows significant vaporization at all of the set point temperatures used in these experiments. The polyphenyl ethers 5P4E and 4P3E give residues of less than 5 percent at all temperatures studied when the time of degradation was long enough for the weight percent of residue to become constant. The lowest molecular weight sample, 3P2E, generated residues of about 15 percent for the intermediate temperatures used. Evaporation of the 3P2E was rapid and the amount of residue became constant after only 5 hours at temperatures of 300°C and higher.

Comparison of the results of the degradation of the polyphenyl ethers with that of the ester-based lubricants shows that the polyphenyl ethers 4P3E and 5P4E form smaller deposits than the ester-based oils. The polyphenyl ether 3P2E left a residue that was comparable to the residues formed by the 3 cSt ester-based lubricants. A possible explanation for this is that the higher molecular weight polyphenyl ethers have a greater resistance to oxidation than the ester-based lubricants and the 3P2E ether. This may enable them to evaporate before significant degradation occurs.

All samples darkened significantly and their viscosities increased noticeably during the time periods where the primary weight loss resulted from evaporation. This indicates that some degradation was occurring during this stage of the treatment. Since all of the samples heated above 300°C produced very small amounts of residue, it is possible that the degradation products are sufficiently volatile to be driven from the sample at these temperatures and not be a part of the final residue. Another possibility is that the effect of the small amount of residue being generated in the 4P3E and 5P4E samples has a large effect on the viscosity and color of those samples while the 3P2E samples heated above 300°C evaporate too quickly for

any significant amount of degradation to occur.

Several different samples of 5P4E were tested. Tables 6 and 7 list the data for the degradation of 5P4E, 5P4E with antioxidant additive and reclaimed 5P4E at 350°C and 375°C. These samples formed essentially identical amounts of residue, indicating that at these temperatures the additive and the degradation material present in the initial samples do not affect the amount of residue formed.

Table 6. Weight Percent Residue, 5P4E, 350°C

Time (hr)	5P4E	5P4E w/antioxidant	5P4E reclaimed
15	44.61	45.75	47.53
20	26.85	30.39	31.36

Table 7. Weight Percent Residue, 5P4E, 375°C

Time (hr)	5P4E	5P4E w/ antioxidant
5	57.36	59.24
10	21.09	20.55
12		8.97
15	5.52	2.24
20	5.01	
25		1.31

SECTION IV

CONCLUSIONS

The MCRT shows good potential as a tool to analyze for carbon residue for lubricant samples that do not tend to evaporate before undergoing degradation. Comparison of the results from the MCRT and a static coker showed similar patterns for the amount of residue produced although the actual percentages varied from one system to the other. Precautions should be taken to ensure that the sample temperature is known since each of the units used showed a difference between the temperature registered on the microprocessor and the temperature of the sample as determined by an iron-constantan thermocouple. The variation was not uniform from unit to unit.

The polyphenyl ethers showed some degradation as evidenced by increased viscosity and discoloration during the early stages of the treatment. The degradation products were evidently volatile enough to be evaporated at temperatures above 350°C. In general, the polyphenyl ethers studied showed resistance toward degradation and displayed a tendency to evaporate rather than degrade at the temperatures studied. To get an accurate picture of the degradation of these materials, one must devise a method that will limit the evaporation losses. The MCRT does not lend itself to this type of modification, and, therefore, may not be the best instrument available to evaluate the residue forming tendency of polyphenyl ethers or other materials that show significant resistance to degradation.

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